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I, JONNE YABSLEY, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2002953190 for a patent by COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION as filed on 09 December 2002.



WITNESS my hand this
Twenty-fourth day of December 2003

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A U S T R A L I A

Patents Act 1990

PROVISIONAL SPECIFICATION

for the invention entitled:

"Aqueous Coating Solutions and Method for the Treatment of a Metal Surface"

The invention is described in the following statement:

AQUEOUS COATING SOLUTIONS AND METHOD FOR THE TREATMENT OF A METAL SURFACE

The present invention relates to an aqueous coating solution and methods for the treatment
5 of a metal surface. Metal surfaces treated with such solution compositions and/or by such
methods are also provided.

More particularly, the invention relates to solution compositions which provide corrosion
resistance to metal surfaces by forming a silicate network on the metal surface which has at
10 least some Si atoms of the silicate network replaced by other metals ions having a valence
of less than or equal to +4. This replacement imparts ion-exchange abilities to the network
and helps maintain surface charge down to low pH values of around 3 (Iler, 1979). These
properties lead to a number of significant advantages and in particular they permit the
incorporation of additional metal cations into the network.

15 The coating of metal surfaces to impart corrosion resistance to the substrate is known. So
called "conversion coatings", and in particular chromium conversion coatings have been
used for corrosion protection of iron, magnesium, aluminium, zinc and their alloys for over
50 years (Cotell et al., 1999). Conversion coatings are generally easily applied, are
20 applicable to a wide range of metals and alloys and under certain conditions provide
excellent adhesion for primers and paints.

Chromate conversion coatings are generally superior in their corrosion protection as they
have a "self-healing" nature (Zhao et al., 2001). That is, they provide active corrosion
25 protection. Chromate conversion coatings provide active corrosion protection in that
chromium(VI) is released from the coating, a mixture of hydrated amorphous Cr(III)-
Cr(VI) oxides, transported through the corrosive solution as soluble Cr(VI) oxy-anions,
and reduced at the site of the damage. Active corrosion protection is critical where the
conversion coating is the primary protection against corrosion. Such protection is
30 maintained even if the treated surface is subject to minor mechanical or chemical damage.

However, chromium is considered a toxic substance, the hexavalent form being a known carcinogen which is environmentally hazardous as a waste product. Indeed, current legislation is moving towards the total exclusion of Cr(VI) and its use in the metal finishing industry is therefore limited. As a result, moves have been made to develop 5 chromium free conversion coatings, including coatings based on silicates, zirconium, titanium, cerium, phosphates, permanganates and hydrotalcites (Gray, 2002). Unfortunately, few of these coatings exhibit comparable corrosion protection to chromate based systems and their use has therefore been limited to some extent. Among the most promising candidates being considered as active corrosion inhibitors are cerium 10 compounds, permanganates, molybdates, vanadates and phosphates (Sinko, 2001).

It has been found that sealed complex oxides, such as Ce or Mn sealed lithium-hydrotalcite, can exhibit active corrosion protection on aluminium alloys (Buchheit et al., 2000). However, rare earth conversion coatings have generally relied on the role of the 15 rare earth in inhibiting the cathodic reaction, and to a lesser extent forming a stable oxide (Hinton, 1995).

Advantageously, the present invention is able to treat a metal surface to establish a coating that provides a predetermined surface chemistry that improves corrosion resistance. 20 Further, the invention advantageously provides methods that may be used in existing treatment facilities and existing treatment baths with minimal alteration to those facilities.

According to one aspect of the invention there is provided a solution composition for providing a corrosion resistant coating to a metal surface. The coating solution includes a 25 water soluble silicate and at least one metal ion (X) selected from those having a valence of less than or equal to +4, which then forms an aqueous silicate-X network such that the silicate remains soluble. When a metal surface (Y) comes in contact with this solution a coating consisting of silicate-X and Y is formed in part because of the ion-exchange properties of the silicate-X network.

Generally speaking, the coating layer provides the surface of the substrate with a predetermined pH_{IEP} , being the pH where the net surface charge is zero as measured by IEP (Isoelectric Point), such that at pH values greater than the pH_{IEP} the surface is negatively charged and will therefore repel negatively charged ions. If a variation occurs in 5 the cross-sectional composition of the coating, it should be controlled so that the pH_{IEP} of the coating is lowest at the atmosphere-coating surface and highest at the coating-metal interface. Preferably the coating solution is composed such that the resulting coating layer on the metal surface has a pH_{IEP} of less than about 3 (at the atmosphere-coating interface) such that with surface waters at a pH of greater than 3 the coated surface of the metal is 10 negatively charged. Even more preferably, the resulting coating layer has a pH_{IEP} of less than 2.5.

It has been recognised by the present inventors that the coating solutions, as outlined, 15 create a coating over the metal surface that provides a negative surface charge at most pH values, particularly at pH values greater than 3 and in some embodiments as low as 2 – 2.5. It is noted in this regard that acid rain has a pH of about 3. As the charge on the coated metal surface is negative at pH values above the pH_{IEP} , negatively charged species in the surface water, such as chloride, sulfate and nitrate ions, are repelled by the surface (Kendig, 1999; Sato, 1989). This helps inhibit corrosion of the substrate. The magnitude of 20 the negative charge on the coated surface at pH 3 becomes larger as the pH_{IEP} is lowered, resulting in stronger repulsion of corrosive negative ions. Typical pH_{IEP} values of common phosphate and chromate(III) chemical conversion coatings are in the range of 5.6 and 7.0, respectively (Reinhard, 1987 ; Sato, 1989).

25 The water soluble silicate is not particularly limited in its selection provided that it is capable of forming a network which may exchange at least some of the Si atoms with metal ions X. Preferably, the water soluble silicate is selected from an alkali metal or ammonium silicate, meta-silicate, ortho-silicate, pyro-silicate, waterglass, silicic acid, silica, colloidal silica, silicon dioxide or an organic-silicate precursor. More particularly, 30 the silicate is preferably selected from the group consisting of sodium silicate or potassium silicate from the practical point of view.

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Similarly, the selection of the metal ion X is not particularly limited, provided that the metal ion has a valence of less than or equal to +4, and can be incorporated into the silicate matrix. Preferably, the metal ion is of an element selected from the group consisting of Al,

5 B, Zr and Ti.

The coating solution may have a concentration of water soluble silicate from 1 ppm to the dispersion limit and a ratio of X to Si from 4:1 to 1:100. Preferably the ratio of X to Si is from 1:1 to 1:50.

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In a particular preferred embodiment, the solution composition includes one or more optional additional components as a potential "active" corrosion inhibitor, preferably selected from the rare earths (lanthanides) or the transition metals (as defined in Cotton et al., 1999), such as but not limited to Ce, Mo, W, Mn or V, but most preferably Ce. It has 15 been found that additional ions such as cerium ions assist in balancing the ion exchange abilities of the metal ion X substituted silicate in aqueous solution and are incorporated into the coating structure in such a way that the cerium ions are held within the coating until coating breakdown occurs. However, some of the bound cerium is able to be ion-exchange and therefore provide active corrosion protection.

20

According to another aspect of the present invention there is provided a method for the treatment of a metal surface, including applying to the metal surface an aqueous coating solution containing a water soluble silicate and at least one metal ion X selected from those having a valence of less than or equal to +4, thus forming a coating layer on the metal 25 surface having a silicate network with at least some of the Si atoms in the silicate network being replaced with said metal ions X and incorporating metal ions Y from the metal surface being coated.

The various options as discussed above relating to the solution composition of the 30 invention also apply to this aspect of the invention.

In one particular embodiment, the treatment of the metal surface includes applying to the metal surface an aqueous solution comprised of silicate ions and aluminium ions to coat the surface of the metal substrate with an aluminosilicate coating. In this embodiment, the metal surface preferably includes a zinc-containing metal surface, which may be zinc, a 5 zinc alloy or a galvanised metal surface. In this embodiment, as the aluminosilicate coating binds to the metal surface, zinc ions may diffuse into the aluminosilicate coating structure so as to form a matrix including silicate ions, aluminium ions and diffused zinc ions. It is also envisaged that other metal substrates may provide a similar mechanism for providing a preferred corrosion resistant coating. For example, the metal surface may include 10 aluminium, magnesium, copper, iron, titanium or their alloys. The metal surface refers to the surface of the metal, an alloy of the metal or a metal or its alloy coated on a different substrate.

According to one embodiment, an aluminosilicate coating having a pH_{IEP} from 2 to 2.5 is 15 applied to the metal surface from an aqueous solution containing silicate ions and aluminium ions. This may be achieved by any suitable means. For example by spraying, painting or dipping. In a preferred embodiment, an aqueous solution comprised of silicate ions and aluminium ions, and further including Ce(IV)/Ce(III) ions as an optional additional corrosion inhibitor, is applied to the metal surface. In one embodiment, zinc 20 metal, or zinc containing metal, is dipped in the above solution. This results in the production of zinc ions at the metal surface forming a diffusion layer. The pH in the diffusion layer near the metal surface rises and results in the formation of an aluminosilicate coating on the metal surface. The zinc ions in the diffusion layer are incorporated into the aluminosilicate coating to form a stable matrix comprised of 25 aluminium, silicon, zinc, and cerium.

Thus, according to a preferred embodiment of the invention, the method includes dipping a zinc-containing metal in an aqueous solution comprised of silicate ions and aluminium ions, and optionally including cerium ions, to form a diffusion layer at the metal surface, 30 and for a time sufficient for an aluminosilicate coating to form on the metal surface. The

aluminosilicate coating including within its structure zinc ions diffused from the zinc-containing metal surface, and optionally cerium ions.

According to another embodiment, an aqueous solution comprised of silicate ions and 5 aluminium ions, preferably containing cerium ions, is prepared and a galvanized metal surface, such as galvanized steel, is dipped into a bath of the aqueous solution. Preferably, the galvanized metal surface is a freshly galvanized metal surface straight out of the molten zinc bath and quenched in the aqueous coating solution. The aqueous coating solution being used as a quench bath for the hot galvanized item. The aqueous coating 10 quench bath is thereby heated upon dipping of the hot galvanized substrate into the bath. The above-described mechanism including diffusion and incorporation of zinc ions into the aluminosilicate coating is considered to hold true according to this embodiment of the invention.

15 An example of the coating composition that results from a preferred embodiment is $\text{Al}_{(a)}\text{Si}_{(b)}\text{Zn}_{(c)}\text{Ce}_{(d)}\text{O}_x$ where $0 < a \leq 1$, $0 < b \leq 1$, $0 < c \leq 1$, $0 \leq d \leq 1$ and $a+b+c+d = 1$, with the overall concentration of the aqueous components ranging from 1ppm to 20wt%.

According to a further aspect of the invention there is provided a metal surface having an 20 aluminosilicate coating, the coating further including diffused metal ions, which have diffused from the metal surface into the aluminosilicate coating during application of the coating to the metal surface. The coating that results has a pH_{IEP} of less than 3.5 at the atmosphere-coating surface and is thus capable of repelling anions in surface water of pH values greater than 3.5.

25 It will be understood that this aspect of the invention follows from the above-described methods of treatment and coating. As such, the preferred features as described above also apply to this aspect of the invention.

In this regard, in a particular embodiment, the metal surface includes a zinc-containing surface and the aluminosilicate coating preferably includes cerium ions as an optional additional corrosion inhibitor.

5 An embodiment of the invention will now be exemplified in more detail. This example is only provided for exemplification only and should not be construed as limiting on the invention in any way.

EXAMPLE

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The performance of a cerium containing, alumino-silicate coating was determined in both neutral salt spray and stack tests. The coating used was a 0.1% solution in water with an elemental ratio of 1:1:5 with respect to Ce, Al and Si. The NSS test was according to AS 2331. While the "stack" test was an industrial specification with the following details. Two 15 sets of paired plates are stacked together and placed in a 100% RH chamber and cycles between 25°C (6 hours) and 10°C (2 hours) for 30 cycles (240 hours). In table 1 and 2 the results for the NSS and the salt tests are given. In the case of NSS no of pits visible to the naked eyes and mass loss is given. Ratio of Mass loss to the mass loss of a zinc blank is also given. Chromate quench was carried out in a 500 ppm solution. The plates in all cases 20 were 10cm x 15cm, and 1mm thick. The results demonstrates that in all cases the CSIRO quench gave performance that matched the chromate quench while both preformed very significantly better than the uncoated galvanised steel or zinc.

Table 1 . Performance in NSS, AS 2331

	NSS Hours	Average Pits/Plate	Average Mass Loss (g/m ² /day)	Ratio of Mass Loss to Blank
CSIRO Quench On Galvanised Steel	72	No Pits	2.7	0.08
CSIRO Coating On Zinc	500	No Pits	5.2	0.33

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Blank Zinc	500	70	15.6	1.00
Chromate Quench on Zinc	72	3	4.0	0.12
Chromate Quench On Zinc	500	5	5.8	0.37

Table 2. Performance in Industrial Stack Test.

Coating	Mass Gain (mg)
CSIRO -quench on galvanized steel	1.5
Chromate quench on galvanised steel	2.0
Water	49.6

5 It is to be understood that, while the preferred embodiments of the invention have been described, it should be appreciated that the invention is susceptible to modifications without departing from the spirit or scope of the invention.

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